Novel Dinuclear Dihydride Complexes of Ruthenium containing Bridging Carboxylate Ligands

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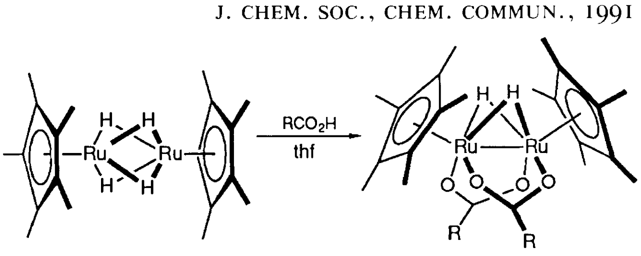
The dinuclear tetrahydride-bridged ruthenium complex $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ reacts with carboxylic acid RCO_2H (R = H, Me, CF_3, C_6H_5, adamantyl) in tetrahydrofuran (thf) to afford the novel dinuclear dihydride complexes $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2(\mu\text{-}RCO_2)_2Ru(\eta^5\text{-}C_5Me_5)$ containing two bridging carboxylate ligands, the reactivities and the X-ray crystal structure of which are also reported.

In our recent work,[1–3] we demonstrated $C(sp^2)$–H and P–C bond activation through the reaction of the dinuclear tetrahydride-bridged ruthenium complex, $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ **1**, with ethene and triphenylphosphine. We also reported that the tetrahydride **1** reacted with trifluoromethanesulphonic acid in benzene to give the cationic 18-electron complex, $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_6H_6)](CF_3SO_3)$.[1] This result implied that protonation of the tetrahydride **1** generated a coordinatively unsaturated species *via* an intermediary cationic polyhydride complex. There have been some reported examples of dihydrogen complexes derived from classical hydride complexes by reaction with protons.[4] We report herein the synthesis of novel dinuclear ruthenium dihydride complexes, $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2(\mu\text{-}RCO_2)_2Ru(\eta^5\text{-}C_5Me_5)$ **2**, by the reaction of **1** with carboxylic acids, and preliminary reactivity studies on these complexes.

Reaction of **1** with an excess of CF_3CO_2H in thf at ambient temperature afforded $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2(\mu\text{-}CF_3CO_2)_2\text{-}Ru(\eta^5\text{-}C_5Me_5)$ **2a** as a red-orange crystalline solid in a 98% yield. Carboxylic acids, RCO_2H [R = H, Me, Ph, adamantyl (Ad)], analogously react with the tetrahydride complex **1** to yield the corresponding dinuclear dihydride complexes **2b–2e** in high yields (Scheme 1). Whereas the reactions of **1** with CF_3CO_2H, HCO_2H and $AdCO_2H$ resulted in the quantitative formation of **2**, the reaction of **1** with $MeCO_2H$ or $PhCO_2H$ gave a 70/30 mixture of **2** and a cationic hydride complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2]_n(RCO_2)_n$ **3a** and **3b**. The structures of **2a–2e** and **3a, b** are based on IR and NMR spectroscopy.†

The ^1H NMR spectrum of **2a** measured in CD_2Cl_2 at room temperature revealed two singlet peaks attributable to the C_5Me_5 and the bridging hydride ligands at δ 1.72 and −4.50, respectively. The ^1H NMR spectrum of **2a** obtained at −50 °C was essentially the same as that measured at room temperature. The inversion-recovery T_1 determination for the hydride ligands in **2a** at −50 °C was performed at 270 MHz by using standard JEOL programs. The observed T_1 value of 251 ms is sufficient to characterize the complex as a classical dihydride complex.

The molecular structure of **2a** was determined by X-ray diffraction studies.‡ The structure of one of the two independent units of $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2(\mu\text{-}RCO_2)_2Ru(\eta^5\text{-}C_5Me_5)$ is shown in Fig. 1. The two ruthenium atoms are quadruply bridged by two hydrides and two carboxylate ligands; the interatomic distance of the two ruthenium atoms is 2.846(2) Å, corresponding to a single Ru–Ru bond. The two μ-carboxylate ligands in **2a** are *cis* to each other in the solid state. The angle between the planes Ru(1)–Ru(1′)–O(1) and Ru(1)–Ru(1′)–O(1′) is 99.8°.



R = CF_3 **2a**, H **2b**, Me **2c**, Ph **2d**, adamantyl **2e**

Scheme 1

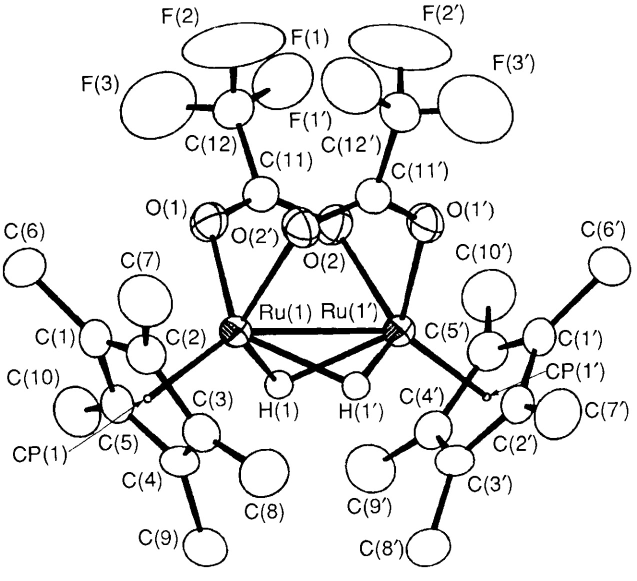


Fig. 1 Molecular structure of $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}\eta^2\text{-}CF_3CO_2)(\mu\text{-}H)]_2$ **2**. Selected bond lengths (Å) and angles (°) are as follows: Ru(1)–Ru(1′) 2.846(2), Ru(1)–O(1) 2.165(6), Ru(1)–O(2′) 2.182(6), Ru(1)–H(1) 2.00(7) 1.97(7), C(11)–O(1) 1.24(1), C(11)–O(2) 1.23(1); Ru(1)–Ru(1′)–O(1′) 81.8(2), Ru(1′)–Ru(1)–O(2′) 81.7(2), Ru(1)–O(1)–C(11) 124.6(5), Ru(1)–O(2)–C(11) 123.9(6), O(1)–C(11)–O(2) 127.7(8). CP indicates the centroids of the C_5Me_5 rings.

Transition metal polyhydride complexes have the potential for creating coordinative unsaturation by the liberation of molecular hydrogen.[5] The carboxylate-bridged dihydride complexes **2** are expected to generate the unsaturated species by the elimination of dihydrogen or carboxylic acids.

Although complex **2** is itself stable both in the solid state and in solution, the Ru–O and Ru–H bonds of **2** are reactive in the presence of donor ligands, and **2** readily generates the coordinatively unsaturated species by addition of CO, C_6H_6 or haloalkanes. Thus, the dihydride complex **2** exhibited interesting reactivity as summarized in Scheme 2. In reactions with neutral ligands such as arenes or CO, they served as 6-electron donors to afford mononuclear cationic 18-electron complexes. Heating a benzene solution of **2a** to 60 °C for 12 h gave $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_6H_6)](CF_3CO_2)$ **4** in a 97% yield as a colourless crystalline solid. The analogous cationic 18-electron complex $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3](CF_3CO_2)$ **5** was obtained in a 95% isolated yield upon treatment of **2a** with 1 atm of CO in thf. The formation of these cationic 18-electron complexes can be reasonably accounted for by the addition of C_6H_6 or CO to the intermediate '$(\eta^5\text{-}C_5Me_5)Ru^+$' derived from **2a** by the elimination of H_2.

The reactivity of **1** toward CO or C_6H_6 is definitely different from that of **2**. The reaction of the tetrahydride complex **1** with CO or C_6H_6 affords a neutral dinuclear carbonyl or diene complex, $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2$ or $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2(\mu\text{-}\eta^2:\eta^2\text{-}1,3\text{-cyclohexadiene})Ru(\eta^5\text{-}C_5Me_5)$, respectively.[7]

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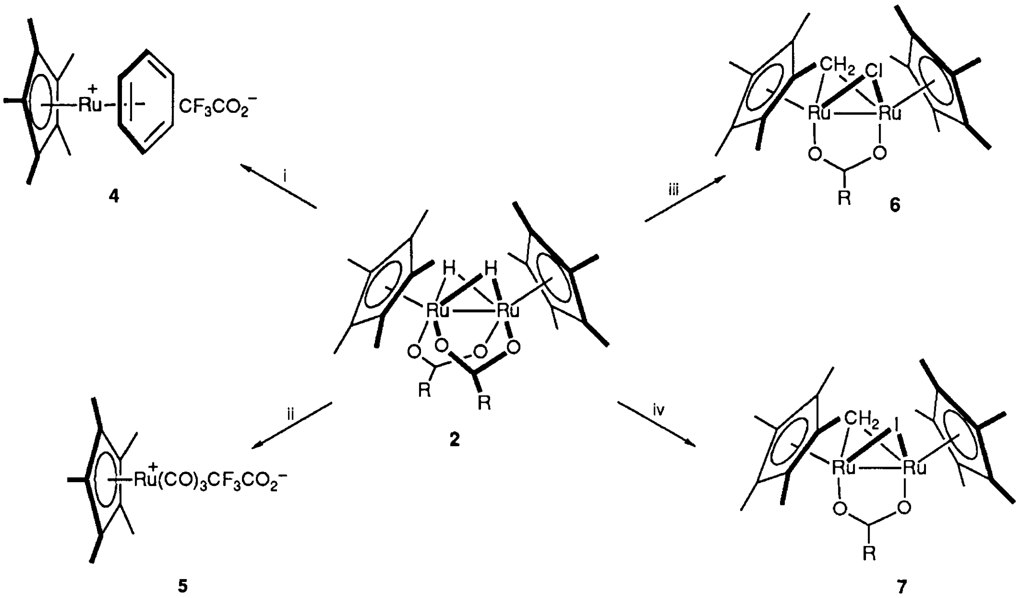
† *Selected spectroscopic data for new compounds.* **2a**: ν_{CO}/cm^{-1} (KBr) 1656; δ_H (270 MHz, $CDCl_3$), 1.72 (30H, s, Cp-Me), −4.50 (2H, s, Ru-H); δ_C (67.5 MHz, $CDCl_3$) 165.8 (CO_2, q, $^2J_{CF}$ 37.5 Hz), 113.7 (CF_3, q, $^1J_{CF}$ 286.8 Hz), 89.2 (Cp-ring), 10.4 (Cp-Me). **2b**: ν_{CO}/cm^{-1} (KBr) 1593; δ_H (270 MHz, [$^2H_8$] thf) 6.75 (2H, s, HCO_2), 1.72 (30H, s, Cp-Me), −4.40 (2H, s, Ru-H); δ_C (67.5 MHz, [$^2H_8$] thf) 170.4 (CO_2), 88.5 (Cp-ring), 10.6 (Cp-Me). **2c**: ν_{CO}/cm^{-1} [(KBr) 1571; δ_H (270 MHz, [$^2H_8$] thf) 1.81 (6H, s, CH_3CO_2), 1.70 (30H, s, Cp-Me), −4.41 (2H, s, Ru-H); δ_C (67.5 MHz, [$^2H_8$] thf) 178.5 (CO_2), 87.9 (Cp-ring), 22.0 (Me), 10.5 (Cp-Me). **2d**: ν_{CO}/cm^{-1} (KBr) 1556; δ_H (270 MHz, [$^2H_8$] thf) 1.84 (30 H, s, Cp-Me), −4.10 (2H, s, Ru-H); δ_C (67.5 MHz, [$^2H_8$] thf) 174.5 (CO_2), 133.6, 130.6, 130.2, 128.0, 88.5 (Cp-ring), 10.7 (Cp-Me). **2e**: ν_{CO}/cm^{-1} (KBr) 1562; δ_H (270 MHz, $CDCl_3$) 1.72 (30H, s, Cp-Me), −4.49 (2H, s, Ru-H); δ_C (67.5 MHz, [$^2H_8$] thf) 184.9 (CO_2), 88.0 (Cp-ring), 41.7, 37.9, 29.8, 10.6 (Cp-Me). **3a**: ν_{CO}/cm^{-1} (in CH_2Cl_2) 1563; δ_H (270 MHz, CD_2Cl_2) 1.98 (15H, s, Cp-Me), 1.73 (3H, s, Me), −11.21 (2H, s, Ru-H); δ_C (67.5 MHz, CD_2Cl_2) 175.3 (CO_2), 98.1 (Cp-ring), 22.3 (Me), 12.3 (Cp-Me). **3b**: ν_{CO}/cm^{-1} (KBr) 1699; δ_H (270 MHz, $CDCl_3$) 1.98 (15H, s, Cp-Me), 7.3–8.1 (5H, m, arom), −11.26 (2H, s, Ru-H); δ_C (67.5 MHz, $CDCl_3$) 169.9 (CO_2), 133.0 (Ph), 130.1 (Ph), 128.3 (Ph), 120.3 (Ph), 97.7 (Cp-ring), 12.1 (CP-Me).

‡ *Crystal data* for **2a**: $C_{24}H_{32}F_6O_4Ru_2$, M = 700.64, orthorhombic, space group *Pccn* (No. 56), a = 16.357(7), b = 15.684(9), c = 21.432(5) Å, U = 5498(6) Å^3, Z = 8 (molecule has a crystallographic twofold rotation axis), D_c = 1.693 g cm^{-3}, λ (Mo-Kα) = 0.71069 Å, μ (Mo-Kα) = 11.43 cm^{-1}, F(000) = 2800, final R value 0.0585, R_w = 0.0763 for 3338 reflections with $F_o - 3\sigma(F_o)$. Intensity data were collected at 23 °C on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo-Kα radiation in the 5° < 2θ < 60° range. Data processing was performed on a Micro VAX II computer by using the TEXSAN crystallographic software package.[6] The positions of the metal atoms were determined by the Patterson method. The positions of all non-hydrogen atoms and two bridging hydrogen atoms were obtained by the sequential difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically by a full-matrix least-squares technique. The bridging hydrogen atoms were refined isotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 2 *Reagents and conditions*: i, benzene, 60 °C, 12 h; ii, CO(1 atm), thf, 25 °C, 3 days; iii, CH_2Cl_2, 60 °C, 30 min; iv, CH_3I, 60 °C, 20 min

A dichloromethane solution of **2c** gave the μ-methylene complex **6** in 70% yield upon stirring at 60 °C for 30 min. The NMR signals for the μ-methylene protons are inequivalent (δ 9.44 and 11.06). The ^{13}C resonance signal for the methylene carbon was observed at δ 175.3 as triplet ($^1J_{CH}$ 140.7 Hz). Interestingly, stirring an iodomethane solution of **2a** at 60 °C for 20 min resulted in the formation of an analogous μ-methylene complex **7**. A possible route to μ-methylene complexes **6** and **7** involves oxidative addition of the halogenated methane, CH_2Cl_2 or MeI, to a dinuclear unsaturated species '(η^5-C_5Me_5)Ru(μ-H)(μ-O_2CR)Ru(η^5-C_5Me_5)' formed by the elimination of RCO_2H from **2**. Complexes **4**–**7** were characterised by means of IR, ^1H and ^{13}C NMR spectroscopy.§

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§ *Selected spectroscopic data for new compounds.* **4**: ν_{CO}/cm^{-1} (KBr) 1692; δ_H (90 MHz, $CDCl_3$) 5.90 (6H, s, C_6H_6), 2.02 (15H, s, Cp-Me). **5**: ν_{CO}/cm^{-1} (KBr) 2031, 1976, 1685; δ_H (270 MHz, C_6D_6) 1.30 (15H, Cp-Me); δ_C (67.5 MHz, C_6D_6) 190.6 (Ru-CO), 169.9 (CO_2, q, $^2J_{CF}$ 35.3 Hz), 115.7 (CF_3, q, $^1J_{CF}$ 290.8 Hz), 99.7 (Cp-ring), 9.2 (Cp-Me). **6**: ν_{CO}/cm^{-1} (KBr) 1545; δ_H (270 MHz, CD_2Cl_2) 11.06 (1H, s, μ-CH_2), 9.44 (1H, s, μ-CH_2) 1.66 (3H, s, CH_3CO_2), 1.60 (30H, Cp-Me); δ_C (67.5 MHz, CD_2Cl_2) 178.3 (CO_2), 175.3 (CH_2, t, $^1J_{CH}$ 140.7 Hz), 86.8 (Cp-ring), 23.6 (Me), 10.4 (Cp-Me). **7**: ν_{CO}/cm^{-1} (KBr) 1638 cm^{-1}; δ_H (270 MHz, C_6D_6) 10.61 (1H, s, μ-CH_2), 9.64 (1H, s, μ-CH_2), 1.53 (30H, s, Cp-Me); 67.5 MHz, C_6D_6) 178.2 (CH_2, dd, $^1J_{CH}$ 134.2 Hz and 140.3 Hz), 166.3 (CO_2, q, $^2J_{CF}$ 37.0 Hz), 113.8 (CF_3, q, $^1J_{CF}$ 287.3 Hz), 87.0 (Cp-ring), 11.2 (Cp-Me).